Biogenic silica and phosphate pools in soils of the North Appalachian Experimental Watershed, Ohio: evaluation of the effects of different agricultural practices

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Abstract

The extent to which human alteration of landscapes affects not only biogeochemical cycles, but also soil and water quality has been shown in many studies. Ohio is home to rich soils derived from glacial deposits and older unglaciated soils, both of which have been extensively utilized for agricultural purposes. This study focuses on small-scale watersheds dominated by agricultural landuse in the North Appalachian Experimental Watershed of Coshocton, Ohio. The watersheds reside in the unglaciated uplands of west-central Appalachia, where residuals soils have been derived from Allegheny Formation siltstones, shales, and sandstones. The site lies within the Muskingham River basin and offers an exceptional arena for study because long term chemical, agricultural and environmental studies have been performed to characterize the site. The sample watershed includes a pasture, conventionally tilled corn, no-till corn without manure, and no-till corn with manure. This study analyzed biogenic silica and phosphate in an area where agricultural practices, especially tilling, are known to enhance erosion and the delivery of carbon to streams.

Samples were collected from depths of 0-70 cm below surface in soils derived from sandstone bedrock. Extractions of SiO_2 and phosphate were done separately on the samples, which were subsequently analyzed with a Skalar SAN++ System autoanalyzer. The nutrients were observed along a depth profile for each watershed, respectively, to evaluate the role of agricultural practices on the biogenic silica (BSi) and reactive phosphate (P) pools, specifically whether till versus no-till practices generate distinct P and BSi signatures, and the potential effects of manure and N-fertilizers. The goal of this study was to quantify BSi and phosphate in the soils and combine these data with previous work on DSi yields, total alkalinity and carbon transport (POC, DOC, DIC) in the same site to elucidate the distinct effects of these land practices and potential trends or relationships. The findings suggest that the application of manure, more so than N-fertilizers, is a large contributor of phosphorous to landscapes. Also, tilling practices are associated with a lower abundance of reactive phosphate and BSi in the soils; however, the profiles suggest that manure application is a stronger control than tilling in depleting soils of amorphous silica.

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Introduction

With the increase of agricultural conversion of landscapes and the increasing awareness of anthropogenic effects on the atmosphere and environment, there arises a need for better understanding the long-term human fingerprint on nature's processes: landscape denudation, chemical fluxes, chemical weathering, erosion, climate feedback, etc. The rise of agriculture is a response to the growing demand of our expanding population for food. Agriculture reshapes the landscape, thereby altering soil properties, hydrology, rates of erosion and chemical weathering (Fortner et al., 2012). Other human activities such as the construction of artificial reservoirs, lakes, dams, and the application of products like fixed nitrogen fertilizers and road salts in urban areas have affected the chemistry of soils, surface and ground waters, and the overall flux of nutrient elements such as silicon, nitrogen, and phosphorous to landscapes. Nutrient saturation and eutrophication of aquatic systems is a threatening response to the increasing anthropogenic delivery of nutrient elements onto landscapes (Carey et al., 2003).

Silicon and oxygen are the two most abundant elements in the Earth's crust, predominantly existing in the form of tetrahedral SiO_4 groups, which is the major constituent of silicate minerals that represent more than 75% of the Earth surface rocks (Borrelli et al., 2010). Silicon is also a crucial element in biogeochemical cycles, where its uses include strengthening cell structures in higher plants and supporting marine cellular structures such as the frustules of diatoms. Thus, the availability of silica plays an important role in the development of soils and of phytoplankton communities in seas. The quantitative analysis of silicon and other nutrients in soil and water is a necessary step in describing landscape loadings and losses.

Silicon has two forms of biological importance: monosilicic acid, the main component of soil solutions, and hydrated amorphous silica. The frustules of diatoms and plant phytoliths are composed of amorphous silica. Frustules and phytoliths are the product of the precipitation of monosilicic acid within cell walls and intercellular spaces, subsequent to the extraction of the acid from surface waters or soil solutions by diatoms and higher plants, respectively (Piperno, 2001). Thus, silicon has biological importance in both the marine and terrestrial environment.

Diatoms are major contributors in primary production, and need dissolved silica (DSi), H_4SiO_4, in larger quantities than other types of phytoplankton; therefore, DSi availability can have a strong influence on phytoplankton community structure and composition in fresh waters and in coastal zones (Harrison et al., 2012). Diatoms incorporate DSi into their frustules, which upon death of the organism sink to sediments and are buried. This process represents the removal of SiO_2 from flowpaths and the sequestration of silica and carbon. Through scientific modeling, estimates have been made which suggest that ecological trapping of SiO_2 is of global importance in SiO_2 fluxes, and that humans have altered river dissolved SiO_2 transport and coastal delivery through construction of reservoirs and dams (Harrison et al., 2012). Previous work in the Alabama River system has identified a decreasing trend for dissolved SiO_2 concentrations (Carey et al., 2003). The removal of DSi by diatom growth and the subsequent sedimentation of diatom frustules in reservoirs has been the attributed cause for the observed trend. Humans are now increasing the number of small lakes, or "reservoirs", on the landscape, the role of which in acting as biogeochemical sinks, particularly for carbon, silica and nitrogen has been increasingly noted through geochemical analyses (Harrison et al., 2012).

The Si cycle is also coupled with the carbon cycle in chemical weathering. Chemical weathering of mineral silicates is the main source of dissolved Si in groundwater (Cornelis et al., 2011), and also has an integral role in the regulation of atmospheric carbon dioxide over geologic timescales. Silicate minerals weathered in carbonic acid release one mole of DSi, while two moles of CO_2 are consumed. This process removes carbon dioxide from the atmosphere and forms carbonate solutes on land, thus causes cooling by lowering greenhouse gas effects (Fortner et al., 2012).

Before silicon makes its land-to-river transfer, it is partially recycled through vegetation. In the soil-plant system, Si becomes mobile, as death and decay of plants lead to a sizable pool of reactive biogenic silica in soils. The significance of this pool of amorphous silica is in the control it has on the release of dissolved silica into soil solution, due to the high solubility of biogenic silica, which is roughly twenty times higher than quartz (Cornelis et al., 2011). Phytoliths are a form of biogenic silica produced by higher plants. They are formed when plants take up dissolved silica in groundwater and incorporate it into their skeletal structures. DSi is taken up through the xylem, a transport tissue in vascular plants (Cornelis et al., 2011). Diatoms form similar siliceous structures called frustules. The frustules of diatoms and phytoliths represent sinks of Si and C in two different environments: marine and terrestrial. The concentration of phytoliths in watersheds may represent a readily available source for the dissolution of silica and introduction of Si into the dissolved phase, more so than crystalline silicates due to the high solubility of amorphous silica. Derry et al. (2005) have shown the significance of biogenic silica in the cycling of Si in groundwater. Their work was done in a mesic tropical, volcanic system where they argue for a strong biological imprint on the silica cycle. They argue, based on germanium and silicon ratios, that much of the silica has been recycled through the biological system. The Hawaiian soils analyzed are generally silica depleted, meaning the biogenic Si pool plays an important role in overall silica fluxes (Derry et al., 2005).

Landscape management presents a challenge for the development of societies. Through geochemical analyses of nutrient loadings and losses, we can better understand the dynamics of element fluxes and apply this knowledge in the future engineering of society, which depends heavily upon the quality of soil, water, ecosystems and atmosphere. The benefit of these studies is long-term. Climate change poses a serious economic threat to many industries, the $300 billion agricultural sector being a primary one. Steps toward conservational practices can mitigate and prevent the costly effects of future mediation needs. Agricultural practices, causing both nutrient saturation and depletion, demand a focused attention regarding the alteration of nutrient cycles. From the 1700s to the 1990s, the conversion of natural into agricultural ecosystems has increased more than six-fold, leading to changes in the hydrologic properties of watersheds, and increased erosion of soils and nutrient fluxes onto landscapes due to manure and fertilizer applications (Fortner et al., 2012). Agricultural landscapes in Coshocton, Ohio have been monitored under government funding for decades. The Ohio State University is currently managing a 75-year database of research from the Coshocton site, and researchers have recently conducted work at this site to strengthen our understanding of the geochemical effects of agriculture (Fortner et al., 2012).

Agricultural practices may retard or enhance the output of DSi and phosphorous (P) to perennial streams, thus causing an anthropogenic disturbance in the Si cycle which is coupled with the fate of organic carbon. Interaction between the Si cycle and the C cycle regulates soil organic carbon sequestration, and the DSi nutrition of phytoplankton carbon dioxide consumers in oceans (Cornelis et al., 2011). An example of agriculturally induced disturbance of silica export can be seen in the Scheldt River Basin, Europe, where the conversion of forested landscapes into agricultural lands for over two centuries has decreased the baseflow export of total silica to the ocean by two to three orders of magnitude (Struyf et al., 2010). Although agricultural practices have been observed to decrease silica export, the conversion of landscapes into agricultural systems sends an initial surge of silica, due to the loss of amorphous silica from soils (Fortner et al., 2012).

The objective of this study was to evaluate the role of agricultural practices on the storage of BSi and P in soils of small watersheds, and to use the wealth of data from the site to strengthen knowledge of the relation of anthropogenic alteration of soil surfaces to hydrologic and chemical parameters. Soil samples from distinct land use-types including tilled corn, pasture, no-till corn with manure, and no till corn without manure were analyzed to quantify the BSi and reactive P pools. Fortner et al. (2012) have conducted research at the site to examine the influence of landuse on hydrology and silicate weathering via N-fertilizers and manures. Huey (2010) recently did work at the site to elucidate landuse effects on carbon fluxes, specifically dissolved organic carbon (DOC), particulate organic carbon (POC) and soil organic carbon (SOC).

Geologic Setting

The landscapes of Coshocton, Ohio represent the unglaciated uplands within the Allegheny portion of the Appalachian Plateau. Soils are largely well drained silt-loam developed from inter-bedded coarse-grained sandstone, shale and limestone (Fortner et al., 2012). Soils there are older than most Ohio soils which were derived from Pleistocene glacial till deposits, and were primarily derived *in situ* from the underlying Pennsylvanian aged shales, siltstones, and sandstones, produced from a previous erosion/deposition cycle and were modified by glaciations older than the Wisconsinan (Fortner et al., 2012). The NAEW lies within the larger Ohio Tennessee River basin and has promise in the potential to extrapolate the area to the rest of the U.S. Corn Belt in terms of monitoring human impacts on landscapes. The northwestern one-fifth of the Ohio-Tennessee River Basin is overlain by till. This till is of mixed lithologies due to the different timing of deposition during Wisconsinan and pre-Illinoian glaciations. The soils of the NAEW originated from earlier glaciations and have correspondingly older soils, which are more resistant to weathering than younger soils of more recently glaciated areas (Fortner et al., 2012).

The NAEW watersheds overlie Paleozoic-aged sediments that lack Pleistocene glacial till (Fortner et al., 2012) .The Berks Series is the predominant soil series in the NAEW. The series consists of well-drained shaley silt loam form from weathered silty shale and siltstone bedrock. The NAEW soils have less than 5 % carbonates and are predominantly composed of aluminosilicates (clay minerals) (Eckstein et al., 2007). Auxiliary soil series in the watershed are the Keene, Rayne and Coshocton silt loam (Kelley, 1975).Soil waters are saturated with kaolinite, illite and gibbsite (Eckstein et al., 2007).

The site is typical of 130,000 km^2 of unglaciated land in southeast Ohio, western Pennsylvania and most of West Virginia, with residual soils developed mainly from flat-lying strata of acid sandstones and shales (Owens et al., 2010). Within the stratigraphy of the landscape, there are nearly impermeable clay layers underlying coal seams. Subsurface water is discharged to the soil surface where theses clay layers outcrop along topography (Owens and Bonta, 2010). The area lacks direct effect from glaciation and the trends of rolling anticlines and synclines can be seen in surface topography where the dip of strata is regionally variable (Kelley, 1975).

Berks Series

The Berks Series at NAEW has been described by Kelley (1975). From a depth of 0-5 inches, the Berks Series contains a shaly silt loam containing many roots and approximately 15% shale fragments. The soil is friable with a weak fine granular structure, bounded by an abrupt smooth surface below. The interval of 5-13 inches is described as a shaly silt loam with approximately 25% shale fragments, friable with many roots, and a weak medium subangular blocky structure. The bottom contact is a clear smooth boundary. The zone of 13-19 inches depth is characterized by a shaly loam commonly with roots, friable, with a medium subangular blocky structure. This zone has thin clay films on the tops of shale fragments. Shale and siltstone fragments make up 50 % of the zone, which is strongly acidic. The bottom boundary of this zone is a gradual smooth boundary. 19-24 inches contains a very shaly loam. It is friable with few roots and thin clay films on shale and siltstone fragments, which make up approximately 55% of the zone. This zone is strongly acidic, and the lower boundary is gradual and smooth. The zone of 24+ inches contains silty shale and siltstone with some fines and sparse clay films in cracks. (Kelley, 1975)

History of Study Site

This study was performed at the North Appalachian Experimental Watershed (NAEW) in Coshocton, Ohio, which provides for a controlled analysis of the effects different agricultural practices in USDA regulated land. The NAEW was established in the 1930's by the Research Division of the Soil Conservation Service, U.S. Department of Agriculture (USDA), to study the relationship of soil, geology, climate, and land use to water flow quantity and quality from natural watersheds. The research area is located west of the Appalachian Mountains, where geology has had a major influence on topography and soil development. The Coshocton site lies within the larger Ohio-Tennessee River Basin which contributed between 33 and 57% of the total annual flow of the Mississippi-Atchafalaya River Basin between 1979 and 2005 (Fortner et al., 2012).

The unglaciated region of the Muskingum River basin consists of primarily cropland, forest and pasture. The NAEW hosts a variety of management practices and land use types including conventional tillage, no-till, pasture, and forest, all coming from the same geological, geographical, and climatic setting. The study analyzed four small watersheds (0.0065 to 0.383 km^2) that are dominated by agricultural land use. Among the sites utilized for animal grazing and crop growth, forested sites can serve as controls, and pastures can be controls for non- crop growth sites. The Coshocton watersheds make for an excellent experimental site because it has been monitored for meteorological, soil and hydrogeochemical conditions for over 70 years (Owens et al., 2010). The area is dedicated to soil and water conservation and has been the site of long-term hydrological data collection under USDA funding since the 1930's. Starting in the 1970's, nutrient and major cation and anion loss data were collected on a regular basis for all watersheds and lysimeters (Owens et al., 2010). The sites have been researched long enough to even begin to reflect a climate change fingerprint, where the growing season has increased 35 days on average during 1979-2007 (Fortner et al., 2012).

Site description

The small watersheds are natural, topographic drainage areas with berms to clearly mark boundaries (Kelley, 1975). The areas of the watersheds range from 0.0065-0.38 km^2.

Watershed 115: Area (0.0065 km^2)

This watershed has been managed by no-till corn practices since 2008, with applications of inorganic N-fertilizers and N-rich manure throughout its 70-year history. The no-till manure treatment involved the application of beef cattle manure at an annual rate of 15 Mg per ha.
The slopes of the watershed range from 2-12%. 115 contains soils developed from shale parent material in the middle and upper part, and has restricted water movement in the B horizon from the heavy texture. Thus, runoff is relatively high, and is enhanced during intense storms and wet conditions. Water is forced to the surface in the lower middle part of the watershed due to an unnamed, discontinuous clay layer near the surface (Kelley, 1975)

N Fertilizer Application (kg*10^3 km^{-2})
1980-1999:139.1
2000-2009: 54.7
1980-1999: 48.2

Manure Application (kg*10^3 km^{-2})
1980-1999: 5400
2000-2009: 1600
1980-1999: 4700
(Modified from Fortner et al., 2012)

Watershed 127: Area (0.0067 km^2)

This site has been managed by disk-tilled corn practices since 2006 and has a 70 year history of N-fertilizer and N-manure applications. The slopes range from 2-18%. Soils at the top of this watershed developed in a silt cap overlying interbedded clay shales and sandstone bedrock (Kelley, 1975) The conventional tilling practice involved moldboard plowing to a depth of 20 cm in November and disking twice before planting in April (Shukla et al., 2004).

N Fertilizer Application (kg*10^3 km^{-2})
2000-20009:70.2
Manure Application (kg*10^3 km^{-2})
2000-2009: 4000
(Modified from Fortner et al., 2012)

Watersheds 115 and 127 both lack base flow, and only have overland flow during storm runoff.

Watershed 182: Area (0.383 km^2)

This site is a pasture, which has been grazed for more than thirty years. There have been no chemical applications to this watershed in the last forty years. This watershed has a permanent stream, thus it has baseflow (Fortner et al., 2012)

Methods

All samples were collected in soils derived from sandstone bedrock in watersheds located within the Allegheny portion of the Appalachian Plateau. Soil phosphorous and silica extractions were performed on the samples. Samples were taken at ten depth intervals from four watersheds each of different land use type.

To collect the soil samples, a backhoe was used to excavate a soil profile from four distinct land types, from which a cross section was cleared off with a shovel. Vinyl gloves were worn while samples were taken from the profile while using a tape measure to record the depth of the sample. Samples were taken at ten depths.

Phosphate:

An acid-fluoride extraction of phosphorous from Dickman and Bray was performed on the samples in which the reagents were ammonium fluoride and hydrochloric acid. To prepare the ammonium fluoride (1N), 37 grams of NH_4F were dissolved in a 1 L solution of distilled water. The solution was stored in a polyethylene bottle. Hydrochloric acid (0.5 N) was prepared by diluting 20.3 mL of concentrated HCl to a volume of 500 mL with distilled water. The extracting solution was made by adding 15 mL of the 1.0 N NH_4F and 25 mL of 0.5 N HCl to a 500 mL volumetric flask filled with water. The resulting solution was 0.03N NH_4F and 0.025 N HCl (Dickman and Bray 1940).

Procedure: The samples were weighed to 5 grams and placed into an extraction container. 25 mL of extracting solution was poured into the container which was shaken for one minute. The contents were then filtered through Whatman No. 42 paper, and poured into "Alpkem" sample cups with filtrate. Samples were then analyzed on a nutrient analyzer.

To report the value as µgrams P per gram sample the following calculation was used to account for the dilution of the sample in 25 mL of extracting solution:

$$\mu\ P/\text{gram sample} = (\text{ppb } P * 0.25)/ (5\ g)$$

Biogenic Silica:

A wet alkaline digestion of SiO_2 from DeMaster (1981) was also performed on samples. Silica was extracted from samples of the four pits ranging from 0-70 cm in depth. The reagents used in the experiment were sodium carbonate and hydrochloric acid. A solution of 0.094 M sodium carbonate was prepared by dissolving 9.96 grams of Na_2CO_3 in distilled water and diluting 1 L. A 0.021 M solution of hydrochloric acid was prepared by diluting 1 mL of 1M HCl with 47.62 mL of distilled water (Demaster 1981).

Samples were weighed (30-60 mg used) and placed in extraction tubes in a hot water bath at 89 ^{o} C. 30 mL of the 0.094 M sodium carbonate was added to each sample to begin the dissolution. Because amorphous silica completely dissolves in the first two hours of the experiment, and crystalline silicates release Si linearly over time, the rate of dissolution of crystalline silicates can be determined and the concentration of ASi can be separated by extrapolating the linear increase of Si from clay minerals to time zero (Figure A).

At three, four and five hours into the dissolution, 1 mL was pipetted from each tube to be analyzed. 9mL of 0.021 M HCl was added to each tube to neutralize the pH for analysis.

Standards of SiO_2 were prepared in polyethylene bottles to calibrate the Skalar San++ System Autoanalyzer. The concentrations of the standards were: 100, 200, 500, 1000 and 2000 ppb SiO_2.The nutrient analyzer was washed out about every ten samples.

After analysis by the nutrient analyzer, corrections were made to account for the dilution of the sample in 30 mL Sodium carbonate, and the 9 mL HCl acid added to the 1 mL decanted solution. To report the value in µgrams BSi per gram of soil the following calculation was used:

µgram BSi/gram sample = ((0.03 * 10 * DSi ppb)/ (weight of sample))

Results

Plots of BSi and P in soils

Plots of BSi versus depth (Figure 1) and phosphorous versus depth (Figure 2) were made for all soils collected.

No-till corn without manure (NTNM): *Watershed 115*

This is the watershed with the highest BSi, ranging 2,500-10,000 µg per g sample.

The range of P is 0.3 to 65 µg per gram sample.

No-till corn with manure (NTM): Watershed 115

The range of BSi concentrations is 1,200-7,300 µg per gram sample. The range of P is 35-145 µg P per gram sample

Tilled corn (T): *Watershed 127*

The range of BSi concentrations for this watershed is 1900-6880 µg BSi per gram sample.

The range of P is 1.7-13 µg P per gram sample

Pasture (P): Watershed 182

The lowest BSi concentrations are found in the pasture. The range of concentrations of BSi was 215-5500 µg BSi per gram sample. The range of P concentrations was 1.4-33.3 µg P per gram sample.

BSi:

Among the watersheds, the no-till corn watershed with manure and conventionally tilled corn watershed have similar ranges of BSi abundances. The pasture has the lowest retention of BSi while the highest pool of BSi was found in the no-tilled corn without manure watershed. With the pasture as a control, an elevated abundance of BSi correlates with crop growth in the remaining watersheds (Figure 1). More DSi is absorbed by plants and deposited as phytoliths upon death and decay of the plants. In comparison with the high levels of BSi in the no-tilled corn without manure, the application of manure in NTM seems to influence a decrease in the abundance of BSi in the soils. Manure may enhance the nitrification of silicate minerals, promoting a more acidic solution to dissolve silicates and export more DSi to streams. Both tilling and manure applications show a signature of lower BSi retention in the soils analyzed in this study. Tilling intentionally disturbs soil compaction and enhances surface runoff, soil loss and erosion. This is likely disturbing the labile BSi pool that resides in the shallow depths of the soil horizon.

The baseline levels of BSi retention in the pasture show that the growth of corn likely influences the Si cycling through small watersheds, due to the uptake of DSi by plants. The pasture experiences no recycling of leaf litter and crop growth, and the soil is compacted from the stocking of cows. The lack of tillage prevents surface erosion, and allows large vertical worm burrows to persist and provide viable pathways for the infiltration of water (Edwards et al.;, 1990). When these burrows are disturbed, there is less infiltration thereby increasing surface runoff and erosion (Edwards et al., 1990). The watershed managed with conventionally tilled corn and N-fertilizer application has higher recorded concentrations of nitrate ions, which may indicate the enhanced weathering of silicates by ammonium (Fortner et al., 2012). N-fertilizers introduce ammonium into the soil, which reacts to produce more protons in the soil solution leading to more oxidation of silicate minerals (Fortner et al., 2012). Thus, increased DSi yields in these watersheds have been attributed by Fortner et al. to the enhanced dissolution of silicates by the application of ammonium which generated nitric acid in soils. The evidence of a smaller pool of amorphous silica in the conventionally tilled corn watershed may correspond to the higher dissolved silica yields observed by Fortner et al., due to enhanced weathering of crystalline and amorphous silica. Thus, the soils are being depleted of BSi and the yields are higher, possibly due to an initial pulse of silica from the loss of the amorphous silica pool.

Phosphorous:

Phosphate has low solubility in soil solutions and is prone to runoff with metal oxides. Phosphate is an anion that forms strong bonds with particles that generate an anion exchange capacity (Cornelis et al., 2011). The elevated concentrations of P in the no-till corn with manure watershed show the strong influence manure application has on affecting the P levels of soils. In comparison with the other land practices that do not involve the application of manure, there is a substantially higher amount of reactive phosphate in the soils of the manure fertilized watershed; a minimum of a two-fold increase due to manure application at each depth interval. The effects of tilling can also be seen in the nutrient phosphate. The tilled corn watershed has a noticeably lower retention of P than the pasture, especially at shallow depths (0-20 cm). Tilling practices are known to increase erosion and to disturb the compaction of soils, leading to a decreased soil matrix density and increased permeability (Owens et al., 2011). This may be why the tilled corn watershed, which receives phosphorous through fertilizer applications, has lower phosphate retention than the pasture. Phosphate may also be exiting the system by the removal of plants during harvest and disk-tilling. The high abundance of phosphate in the pasture, relative to the tilled corn watershed, may indicate that animal occupancy is increasing the delivery of organic phosphate to the landscape through excreta.

Discussion

The data show that labile amorphous silica increases with depth within the watershed. The no-tilled corn without manure and the tilled corn sites show an increase of BSi with increasing depth. The pasture and the no-till corn with manure both show an increase in BSi concentrations to an intermediate depth of approximately 50 cm, at which the BSi abundances level off.

Ohio landscapes have experienced extensive agricultural use because of the rich residual soils developed from glacial till deposits; however, unglaciated regions, which are typical of eastern Pennsylvania and much of West Virginia, have also been managed agriculturally. In the interest of conservation, watersheds in Coshocton, Ohio have been set aside for experimental purposes to determine the effects of different agricultural landuses on soil quality, erosion, infiltration and nutrient cycling. The need to develop observatories in both glaciated and nonglaciated zones is based on the fact that the soils developed in these two locations have different ages, lithologies, and origins, and these factors may relate to chemical weathering fluxes. Geochemical analyses of soil and groundwater can improve our understanding of chemical fluxes, sinks and sources, and aid in improving and conserving soil and water quality. As agriculture intensifies and the global application of fertilizers continues to grow, considerations regarding the anthropogenic disturbances of landscapes and chemical fluxes become more important. Further study will be required to classify the relations between distinct lithologies and landscape age.

The erosional effect of tilling has been observed in this study. Work done by Huey et al. (2010) on the NAEW has shown that agricultural practices, especially tilling enhance the delivery of carbon to streams. Conventional tillage may be the least sustainable practice. Grazing and tilling reduce infiltration and increase surface runoff. Areas used for cattle grazing have been shown to be associated with increased soil loss, surface runoff and carbon losses, both SOC and DOC (Owens et al., 2011). Harvesting crops has been shown to reduce the amount of silica returning to landscapes through the decay of plants (Fortner et al., 2012). Grazing intensity can also affect water quality. A study using dairy cows in the northeast United States found an increased leaching loss of NO_3-N with increasing stocking rates, the attributed cause being urine patches (Owens et al., 2012). In New Zealand, greater losses of nitrogen and phosphorous were measured in surface runoff from high fertilizer catchments compared to low fertilizer catchments (Owens et al., 2012). Owens et al. noted that increased duration of animal occupancy led to increased organic nitrogen and total organic carbon (TOC) in stream flow (Owens et al., 2012).

Conclusions and suggestions for future work

Further work is required to characterize the effects of agricultural land practices on chemical fluxes. The importance of this study was to evaluate unglaciated soils, in order to add to the understanding of the relation of agriculture to specific lithologies and landscape age. The importance of studies of this type grows with our increasing knowledge of human induced climate change. Climate change projections warn us of future problems threatening our society regarding food supply, soil and water quality, etc. Our modern society depends on science to understand climate change and the threats it may pose in the future. The Coshocton site has the promise of scaling small scale watersheds to a larger area to understand chemical fluxes in the Ohio-Tennessee River Basin.

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Appendix A

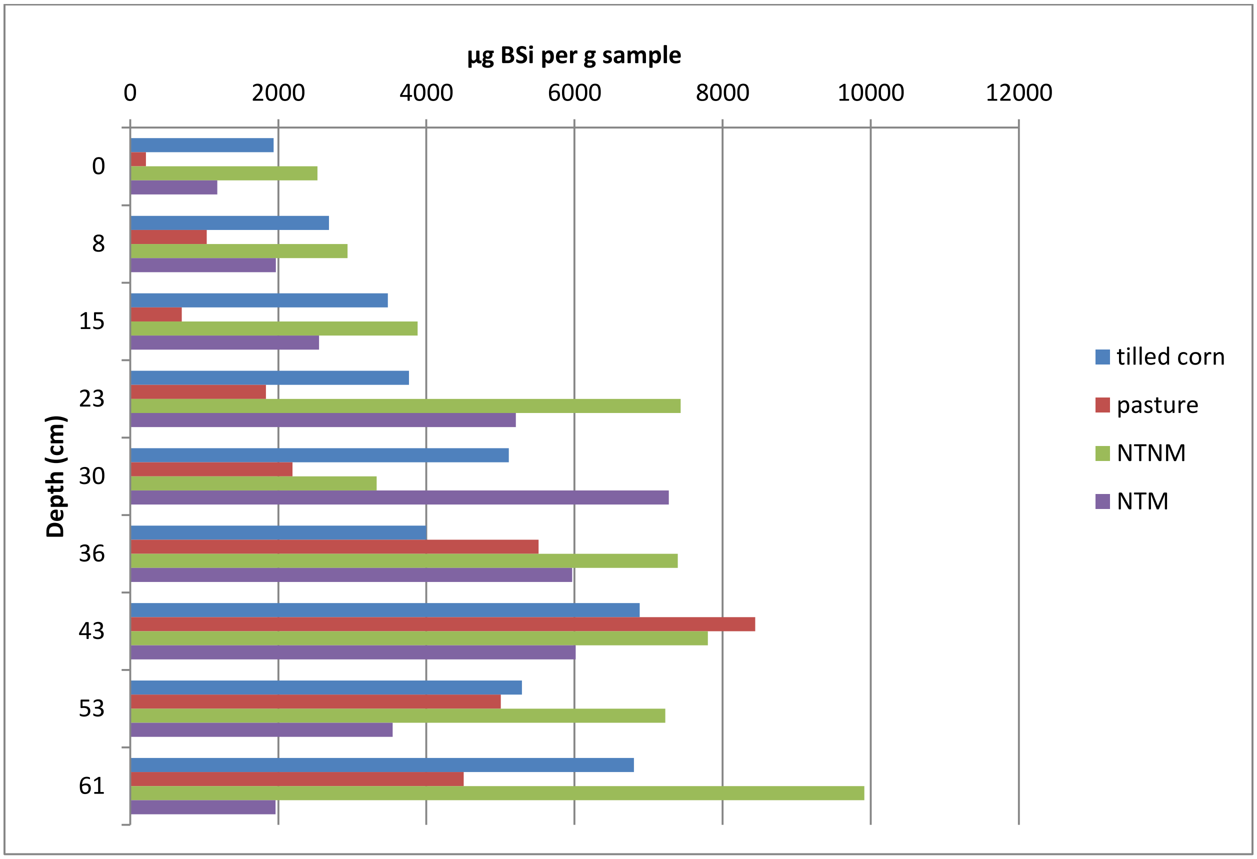

Figure 1. Plot of BSi versus depth for four watersheds

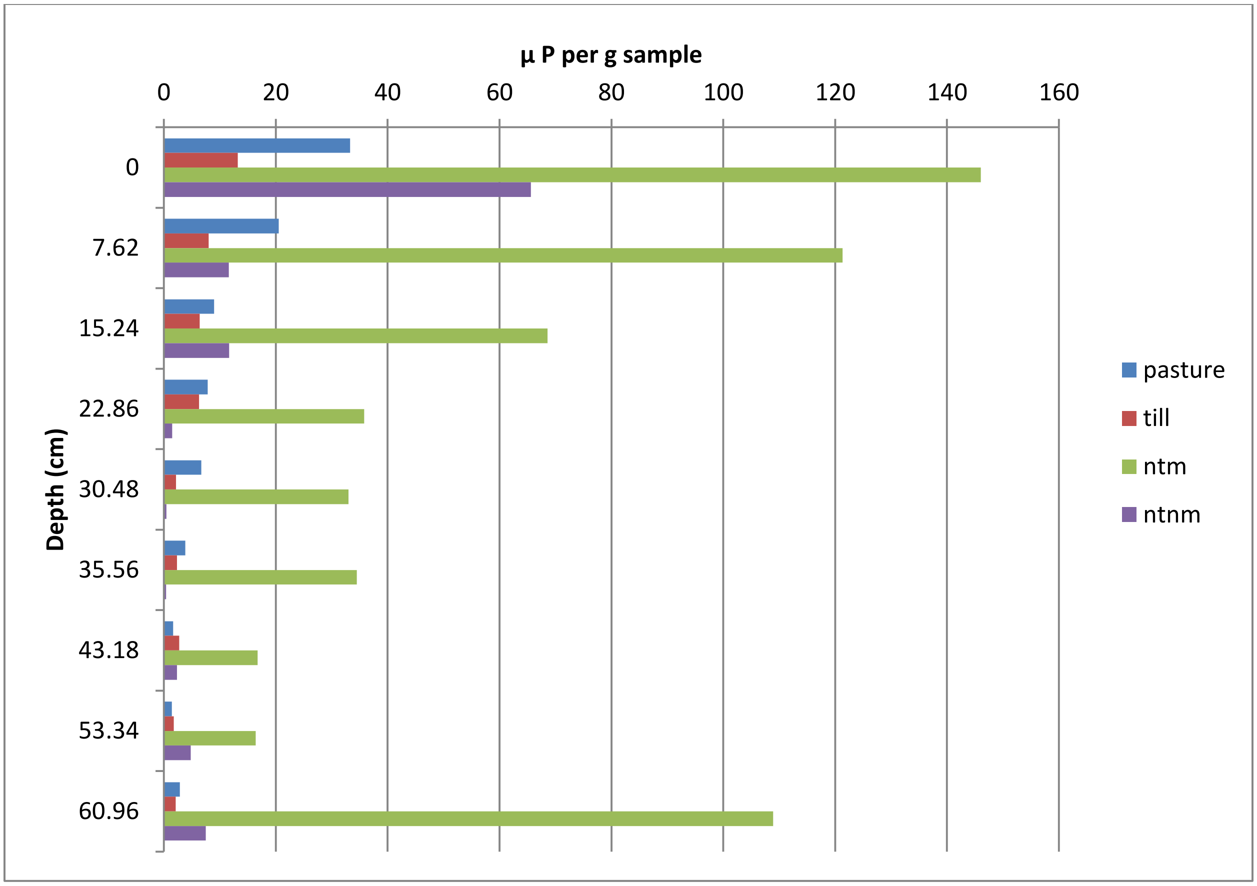

Figure 2. Plot of P versus depth for four watersheds

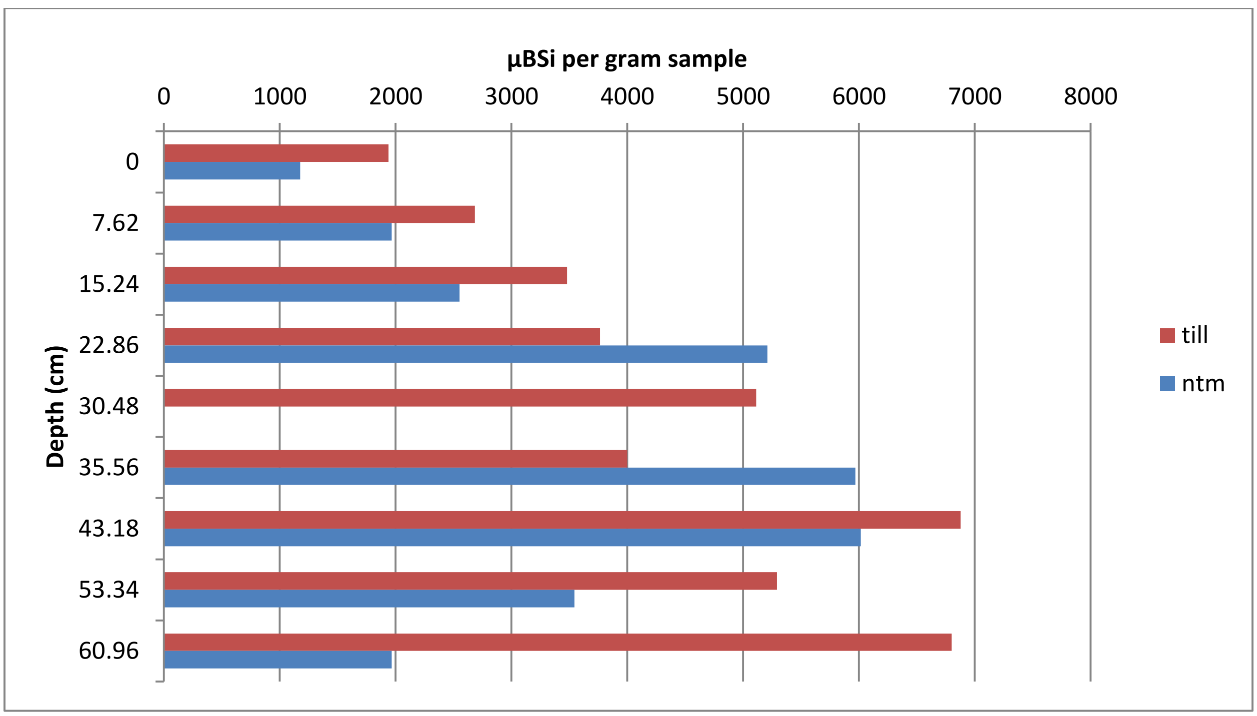

Figure 3. Plot of BSi versus depth for tilled corn watershed and no-till manure watershed

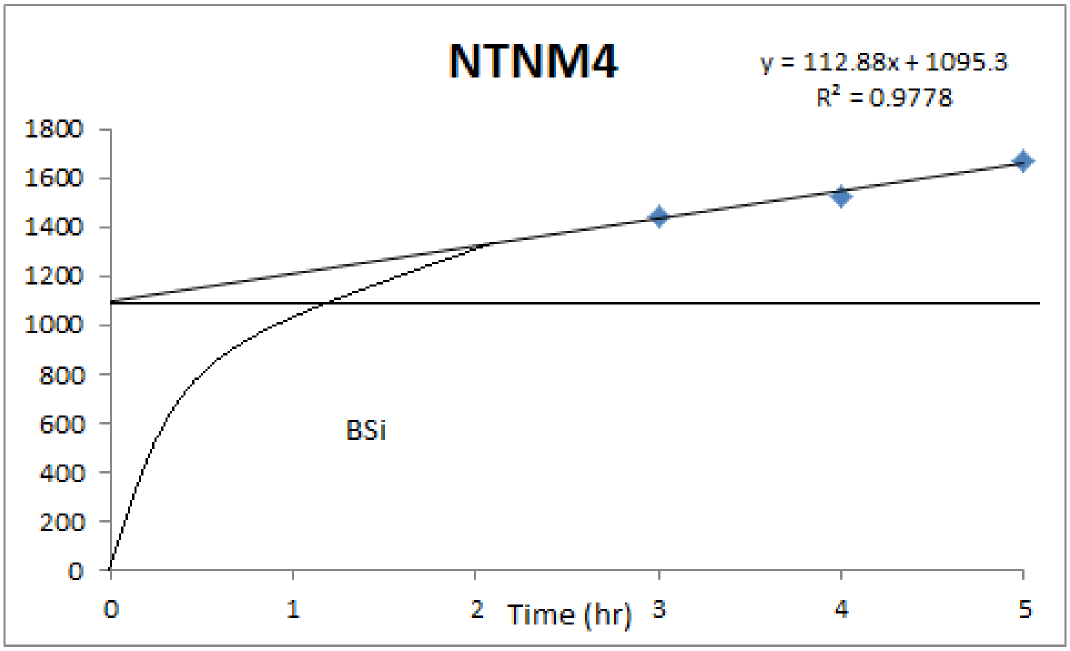

Figure A. Example dissolution curve for determination of BSi concentrations

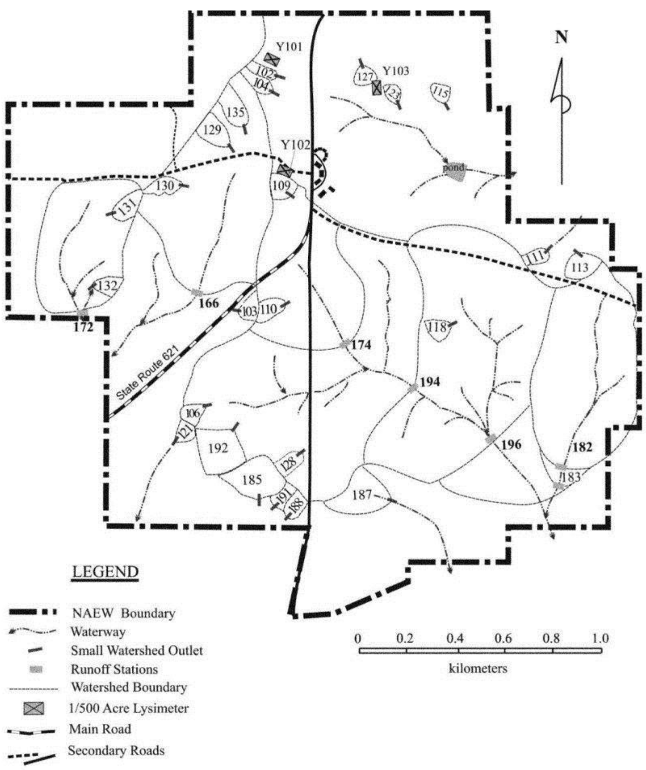

Fig. B. Map of the USDA North Appalachian Experimental Watershed (NAEW) watersheds, Ohio, NAEW watersheds include:
WS 115 Corn No-Till, WS 127
Corn Till, WS 166 Mixed-Use, WS 172 Forest, and WS 182 Unimproved Pasture (modified from Fortner et al., 2012)

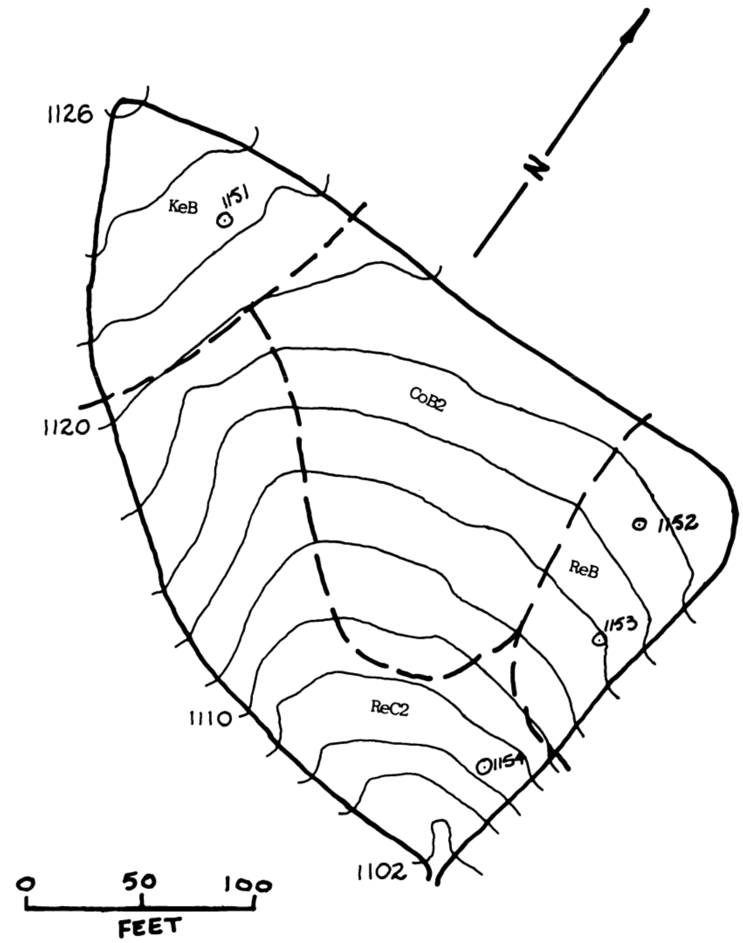

Figure C: map of watershed 115. KeB- Keene silt loam. CoB2- Coshocton silt loam. Re- Rayne silt loam. (Modified from Kelley 1975)

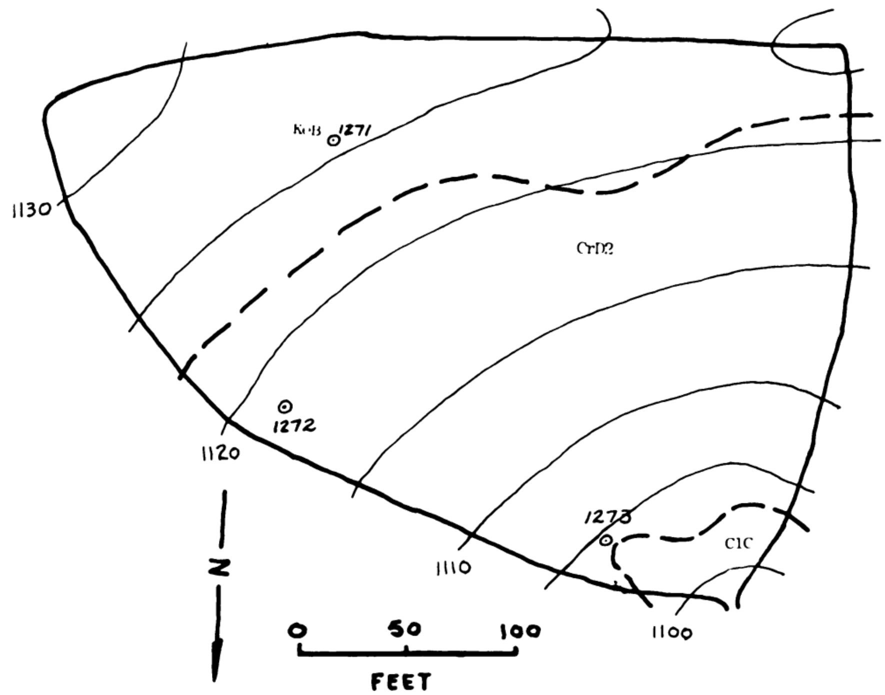

Figure D: map of watershed 127. KeB- Keene silt loam. CrD2- Coshocton Rayne silt loams. (Modified from Kelley 1975)